Solvent effects and acid ion exchange activity in hydration of cyclohexene and methanolation of isobutene.

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Summary

Two liquid-phase acid catalyzed addition reactions have been investigated, i.e. the hydration of cyclohexene to cyclohexanol and the addition of methanol to isobutene giving methyl tertiary-butyl ether (MtBE). In both reactions we used macroporous strong acid ion-exchangers as immobilized acid catalysts.

Cyclohexanol is an intermediate for the production of caprolactam, which is used for the production of nylon-6. Presently, cyclohexane or phenol is often the starting material. There is considerable industrial interest for a new route, which involves the selective partial hydrogenation of benzene to cyclohexene followed by the hydration of cyclohexene. No information is available about the liquid-phase hydration of cyclohexene catalyzed by strong acid ion-exchange resins. Therefore, we carried out a thorough investigation about this reaction to see whether the production of cyclohexanol can be realized on an industrial scale via the hydration of cyclohexene.

Preliminary experiments showed that the very low solubility of cyclohexene in water is responsible for very small production rates per unit volume of catalyst. Strong acid ion-exchangers are very hydrophilic. Therefore, all pores are filled with water, which thus can be considered as the reaction phase.

A possible alternative for obtaining higher production rates is the use of a cosolvent, which results in a single liquid phase and in a greatly improved solubility of cyclohexene in the reaction phase. A proper cosolvent is not easily found. It has to be completely miscible with water and it must be really inert under strongly acid reaction conditions. Moreover, the solvent should not have any proton affinity, which would decrease the acidity of the resin. Sulfolane is one of the few solvents which satisfies all conditions.

Addition of sulfolane will not only increase the solubility of cyclohexene, but also change the equilibrium conversion, the reaction rate and the activity of the ion-exchanger. These changes in thermodynamical properties can be described by changes in activity coefficients of the components present. We used UNIFAC, a group contribution method, to compute activity coefficients of both the reactants and the product in various solvent mixtures.

Measurements of the solubility of cyclohexene in various water-sulfolane mixtures as a function of the temperature are presented in Chapter 2. The solubility increases both with increasing temperature and sulfolane content. Addition of 90 mol% sulfolane to water leads to an increase of the solubility of cyclohexene by typically two orders of magnitude. This increase is due to a strong decrease of the activity coefficient of cyclohexene. Cyclohexene solubilities can be predicted by UNIFAC to within 30%.

Reaction rate constants are given in Chapter 3. It could be experimentally shown that the hydration of cyclohexene follows pseudo-first order reversible kinetics in cyclohexene and cyclohexanol. Further a pseudo-homogeneous model for catalysis by solvated protons appears to describe the observed conversion rates accurately. The rate constant depends on the percentage of sulfolane with a minimum rate constant around 60 mol% sulfolane. The observed solvent effects are explained in terms of changing activity coefficients of both the reactants and the activated complex. Computations showed that a strong stabilization of cyclohexene is almost entirely responsible for the observed decrease in rate constant with increasing sulfolane content until 60 mol% sulfolane. At higher molar percentages of sulfolane the proton activity increases with increasing sulfolane content. This is the main reason for the observed increase in rate constant above 60 mol% sulfolane.

Changes in the equilibrium conversion caused by the addition of sulfolane are presented in Chapter 4. The equilibrium conversion appears to decrease continuously with increasing sulfolane percentage. This could be explained from a stronger stabilization of the reactants relative to the product.

The second reaction studied was the synthesis of MtBE. These investigations were initiated by a MtBE producing company. The catalysts used in the MtBE synthesis have a limited lifetime of approximately 2 years. In the open literature little is known about the relative reactivity of available catalysts.

We examined a number of commercially available macroporous ion exchange resins with respect to the MtBE synthesis. Reaction rate constants were determined as a function of temperature. Effects of the feed composition and of the degree of deactivation on the rate constants and the energies of activation were determined.

The observed changes in the MtBE production rate could be explained in terms of a pseudo-homogeneous rate model in combination with transition state theory.

The effect of reaction mixture composition on the MtBE production rate is presented in Chapter 5. The forward rate constant decreases continuously with increasing isobutene/methanol ratio, whereas an increase in reaction rate constant is observed with an increasing amount of MtBE in the reaction mixture. As far as we know, this effect has not been reported elsewhere. Changes in the activity of the initial state are primarily responsible for the decrease in rate constant with increasing isobutene/methanol ratio. The increasing rate constant with increasing MtBE content mainly stems from changes in the activity of the activated complex.

In Chapter 6 kinetic results are presented for the MtBE synthesis catalyzed by various strong acid ion-exchangers. Despite all ion-exchangers were macroporous and contained similar sulfonic acid groups, significant differences in rate constants were observed. It appeared that the differences in rate constants increased if part of the protons were exchanged by sodium ions. At 10% proton capacity the rate constants per equivalent acid appeared to be reduced by a factor of 9 to more than a factor of 20, depending on the catalyst applied. The temperature at which mass transfer limitations start to occur turned out to vary between 50 and 80 °C, depending on the resin applied.